Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

# Zinc(II) tetraphenyltetrabenzoporphyrin complex as triplet photosensitizer for triplet-triplet annihilation upconversion

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# 1. Experimental Section

## General information

All the chemicals used in synthesis are analytical pure and were used as received. Solvents were dried and distilled before used for synthesis. $^1$H and $^{13}$C NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer (TMS as the standard of the chemical shifts). The mass spectra were measured by a MALDI and ESI Micro MS spectrometer. UV-vis absorption spectra were taken on a HP8453 UV-visible spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu RF 5301PC spectrofluorometer. Luminescence lifetimes were measured on a OB 920 fluorescence/phosphorescence lifetime instrument. The nanosecond time-resolved transient difference absorption spectra were detected by Edinburgh LP920 instruments (Edinburgh Instruments, UK). The signal was buffered on a Tektronix TDS 3012B oscilloscope and was analyzed by the LP900 software. Fluorescence quantum yields were measured with DCM (4-dicyanomethylene-6-(*p*-dimethylaminostyryl)-2-methyl-4H-pyran) as the standard ($\Phi_F = 0.1$ in $CH_2Cl_2$).

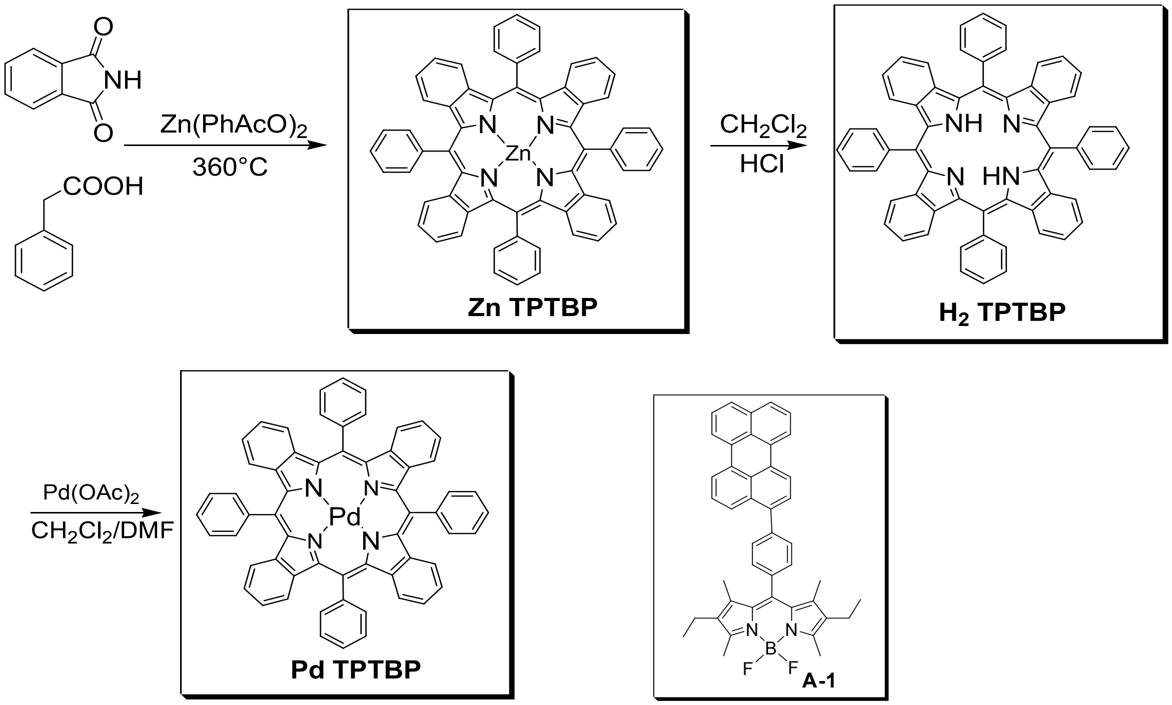
A laser diode (continuous laser, 654 nm,12 mW, 95.5 mW cm$^{-2}$) was used as the excitation source for the upconversion. The power of the laser beam was measured with VLP-2000 pyroelectric laser power meter. For the upconversion experiments, the mixed solution of the compound (triplet photosensitizers) and the triplet acceptors was degassed with $N_2$ for at least 15 min. The steady state upconverted fluorescence was recorded with a RF 5301PC spectrofluorometer. In order to repress the laser scattering, a small black box was put behind the fluorescent cuvette as beam dump to trap the laser.

The upconversion quantum yields ($\Phi_{UC}$) of ZnTPTBP, $H_2$TPTBP and PdTPTBP were determined with the prompt fluorescence of the free porphyrin $H_2$TPTBP as the inner standard, e.g. The upconversion quantum yields were calculated with the following equation (Eq. 1), where $\Phi_{UC}$, $A_{sam}$ and $I_{sam}$ represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the samples. $\eta_{sam}$ represents the diffraction index used for the samples, symbols with 'std' stand the corresponding parameter for the standard (Eq. 1)

$$\Phi_{sam} = 2\Phi_{std}\left(\frac{A_{std}}{A_{sam}}\right)\left(\frac{I_{sam}}{I_{std}}\right)\left(\frac{\eta_{sam}}{\eta_{std}}\right)^2 \qquad \textbf{(Eq. 1)}$$

The delayed fluorescence of the upconversion was measured with a nanosecond pulsed laser (Opolette$^{TM}$ 355II+UV nanosecond pulsed laser, typical pulse length: 7 ns. Pulse repetition: 20 Hz. Peak OPO energy: 4 mJ. The wavelength is tunable in the range of 210 – 355 nm and 410 – 2200 nm. OPOTEK, USA), which is synchronized to FLS 920 spectrofluorometer (Edinburgh Instruments, UK). The pulsed laser is sufficient to sensitize the TTA upconversion. The decay kinetics of the upconverted fluorescence (delayed fluorescence) was monitored with an FLS920 spectrofluorometer (synchronized to the OPO nanosecond pulse laser). The prompt fluorescence lifetime of the triplet acceptor **A-1** was measured with EPL picosecond pulsed laser (405 nm, 405 ±10 nm, pulse width: 66.9 ps, maximum average power: 5 mW; Edinburgh Instrument Ltd., UK) which was synchronized to the FLS 920 spectrofluorometer.

## Synthesis of compounds ZnTPTBP, $H_2$TPTBP, PdTPTBP and A-1



**Scheme S1.** Synthesis of meso-tetraphenyltetrabenzoporphyrin compounds of PdTPTBP, $H_2$TPTBP, ZnTPTPB. The molecular structure of triplet acceptor **A-1** used in the TTA upconversion studies is also presented.

**Zn TPTBP, $H_2$ TPTBP** and **Pd TPTBP** were synthesized according to a modified literature method.[1]

**Synthesis of Zinc phenylacetate**: Sodium hydroxide (2.32 g, 0.058 mol), phenylacetic acid (7.76 g, 0.058 mol) and 40 mL water were mixed together, the pH value was adjusted to 8.0. Then $ZnCl_2$ (4.09 g, 0.03 mol) was dissolved in a small amount of water and the pH value was adjusted to 3.0. With the exchange reaction between sodium phenylacetate and $ZnCl_2$, Zinc phenylacetate was obtained as a white precipitate. The product was isolated by filtration and the product was used without further purification. Yield: 8.59 g (89.8%).

**Synthesis of ZnTPTBP** : The preparation followed a reported method.[1] Under $N_2$ atmosphere, phthalimide (1.47 g, 10.0 mmol), phenylacetic acid (1.80 g, 13.3 mmol) and Zinc phenylacetate (0.840 g, 2.5 mmol) were ground in a mortar and loaded into a 50 mL round-bottom flask. The mixture was melted and stirred for 1 h at 360 °C until the color turned dark green. The melt was collected and washed with water (2×100 mL) and dried over $Na_2SO_4$. The product was dissolved in toluene and purified on column chromatography( $Al_2O_3$). The column was elutated firstly with toluene/hexane (2:1, v/v) and then with toluene to remove the yellow and the red fractions. Finally, $CH_2Cl_2$ containing 1.5% tetrahydrofuran was used to elute the desired product. Yield: 405.0 mg (18.5 %). $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 8.27 (d, 8H, $J$ = 7.2 Hz), 8.03 (d, 4H, $J$ = 8.0 Hz), 7.96 (t, 8H, $J$ = 16.0 Hz), 7.28–7.24 (m, 8H),

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[1] S. M. Borisov, I. Klimant, *Dyes and Pigm*. 2009, **83**, 312–316.

7.08–7.05 (m, 8H). MALDI-HRMS: Calcd ([$C_{60}H_{36}N_4Zn$]$^+$) *m/z* 876.22314, found *m/z* 876.2222. Other peaks: *m/z* 966.2708(ZnTPTBP+$C_7H_7$)) and *m/z* 1056.3065 (ZnTPTBP+2($C_7H_7$)).[1]

**Synthesis of $H_2$TPTBP:** The preparation followed a reported method.[1] ZnTPTBP (50.0 mg, 0.057 mmol) was dissolved in $CH_2Cl_2$ (20 mL) and then 15 mL of hydrochloride acid (HCl:$H_2O$ = 1:2, v/v) was added. The solution was stirred for 30 min. Water (100 mL) was added in the mixture. The mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The solvent was evaporated under reduced pressure, the solid was washed thoroughly with water and dried under vacuum. The crude product was purified with column chromatography (silica gel, $CH_2Cl_2$) to give dark-green powder. Yield: 22.3 mg (48.0 %) .$^1$H NMR (400 MHz, DMSO-d$_6$, ): $\delta$ 8.33 (d, 8H, *J* = 5.6 Hz ), 8.05 (t, 4H, *J* = 16.0 Hz ), 7.97 (t, 8H, *J* = 16.0 Hz), 7.33–7.00 (m, 16H), −1.07 (s, 2H). MALDI-HRMS: Calcd ([$C_{60}H_{38}N_4$+$H^+$]$^+$), *m/z* 814.3097, found, *m/z* 815.3129. Other peaks: *m/z* 905.3795(TPTBP+$C_7H_7$) and *m/z* 995.4377 (TPTBP+($C_7H_7$)$_2$).[1]

**Synthesis of PdTPTBP**: The preparation followed a reported method.[1] Under nitrogen atmosphere, $H_2$TPTBP (30.3 mg, 0.037 mmol) was dissolved in 20 mL solution ( $CH_2Cl_2$:DMF = 1:3, v/v). Then Pd(OAc)$_2$ (24.8 mg, 0.11 mmol) was added. The reaction mixture was refluxed at 150 °C and stirred for 45 min until the UV-Vis absorption spectrum indicated the reaction was finished. The weak absorption at 633 nm disappeared and a new strong absorption at 628 nm emerged. In toluene). After completion of the reaction, the mixture was cooled to r. t. The mixture was evaporated to dryness under reduced pressure, then washed with hot water. The solid was dried under vacuum. The product was dissolved in toluene and purified by column chromatography ($Al_2O_3$, toluene/hexane, 1:1, v/v). Yield: 16.3 mg (47.9 %). $^1$H NMR ( 400 MHz. DMSO-*d*$_6$): $\delta$ 8.25 (d, 8 H, *J* = 7.2 Hz), 8.04 (d, 4 H, *J* = 7.2 Hz), 7.97 (t, 8 H, *J* = 14.0 Hz), 7.30–7.28 (m, 8 H), 7.06–7.03 (m, 8 H). MALDI-HRMS: Calcd ([$C_{60}H_{36}N_4Pd$]$^+$), *m/z* 918.1975, found, *m/z* 918.2038. Other peaks: *m/z* 1008.2810 (ZnTPTBP+$C_7H_7$) and *m/z* 1101.2496(ZnTPTBP+($C_7H_7$)$_2$).[1]

**Synthesis of A-1** : **A-1** were synthesized by a modified literature method.[2] Orange power was obtained. Yield (28.0 mg, 51.2%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.28 (d, 2H, *J* = 7.6 Hz), 8.24 (d, 2H, *J* = 6.8 Hz), 7.73 (d, 3H, *J* = 7.6 Hz), 7.66 (d, 2H, *J* = 7.6 Hz), 7.53–7.42(m, 6H), 2.57 (s, 6H), 2.38 (q, 4H, *J* = 6.8 Hz), 1.48 (s, 6H), 1.04 (t, 6H, *J* = 14.4 Hz). EI-HRMS: Calcd ([$C_{43}H_{37}BN_2F_2$]$^+$), *m/z* 630.3018, found, *m/z* 630.3026.

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[2] A. Turshatov, D. Busko, Y. Avlasevich, T. Miteva, K. Landfester, S. Baluschev, *ChemPhysChem*. 2012, **13**, 3112–3115.

## 2. NMR and MS spectra

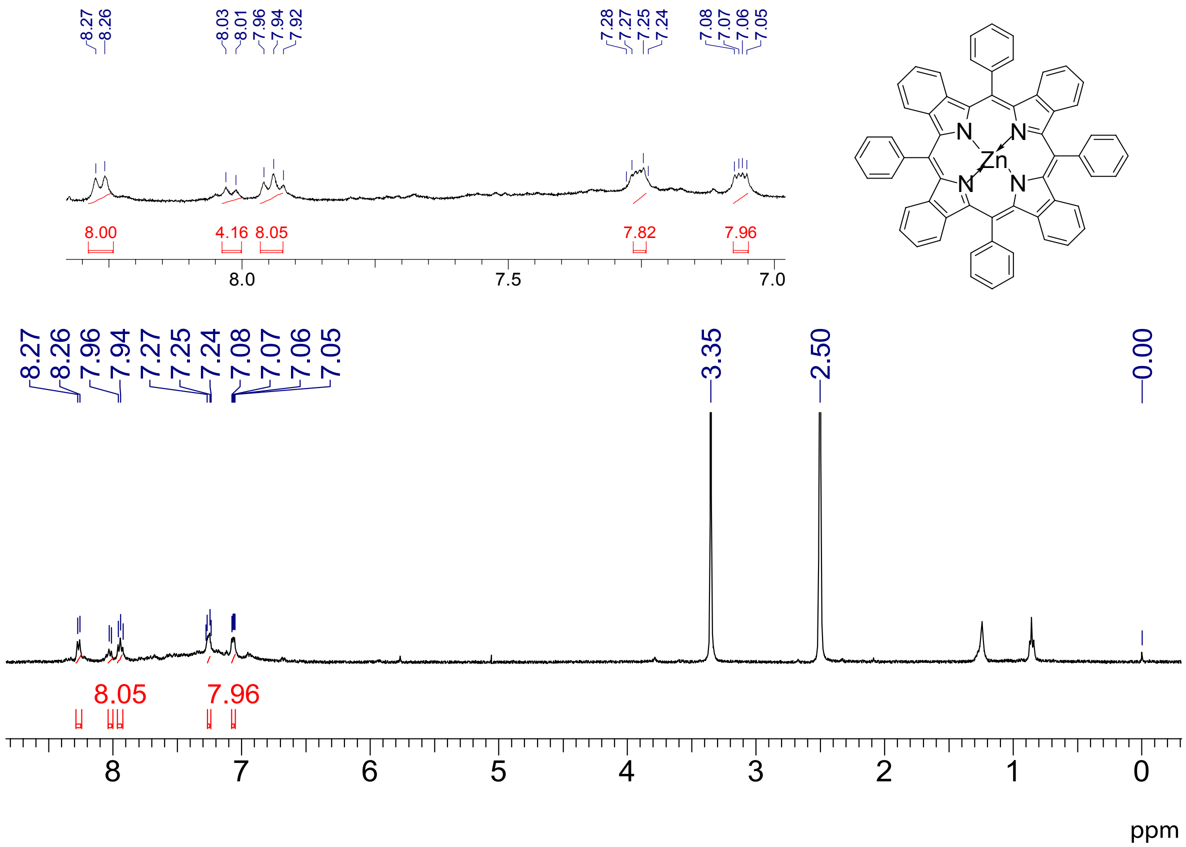


**Fig. S1** $^1$H NMR spectra of **Zn TPTBP** (400 MHz, DMSO-$d_6$).

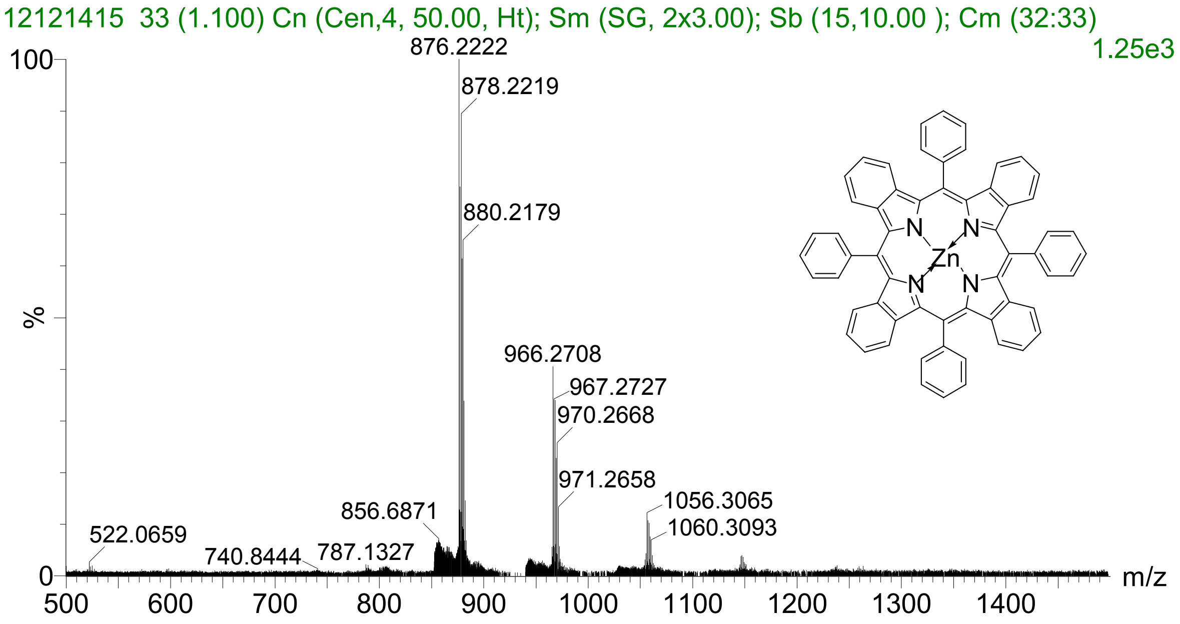


**Fig. S2** MALDI-HRMS of **ZnTPTBP**.

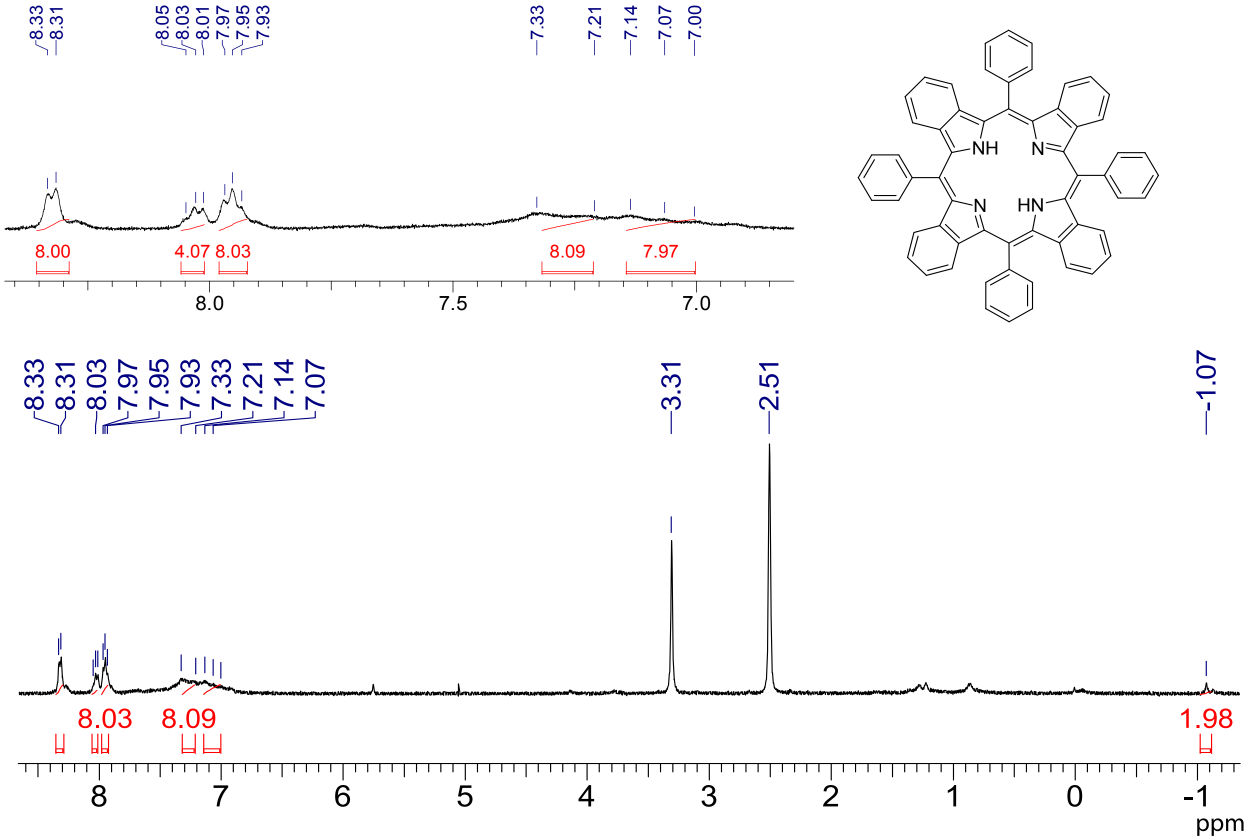


**Fig. S3** $^1$H NMR spectra of **H$_2$TPTBP** (400 MHz, DMSO-d$_6$)

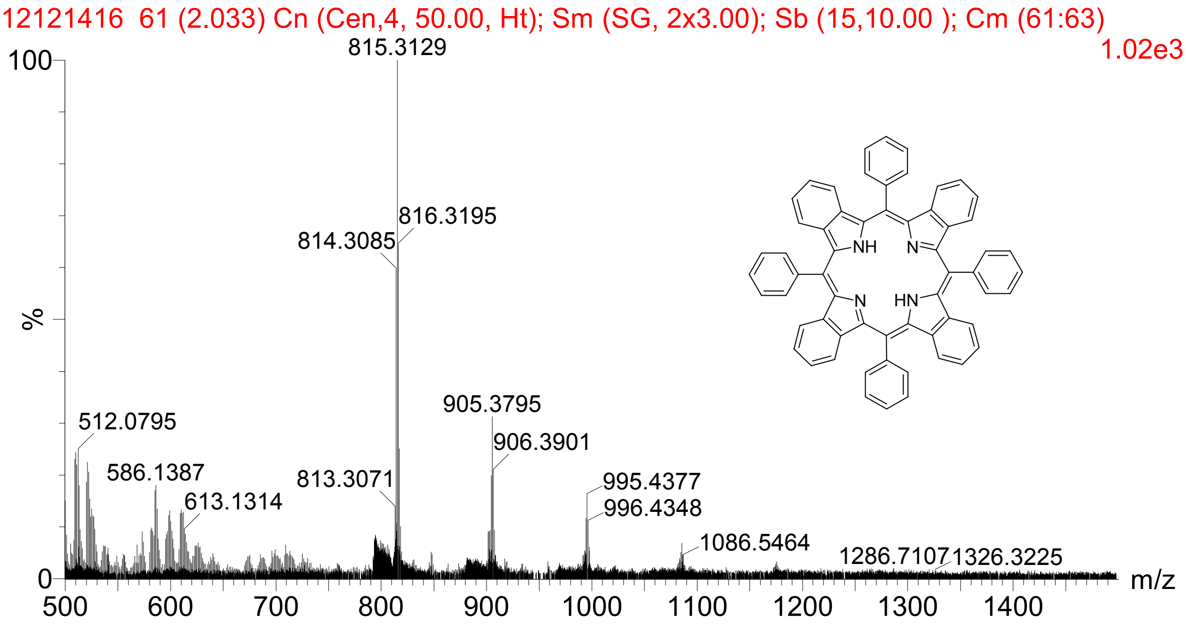


**Fig. S4** MALDI-HRMS of **H$_2$TPTBP.**

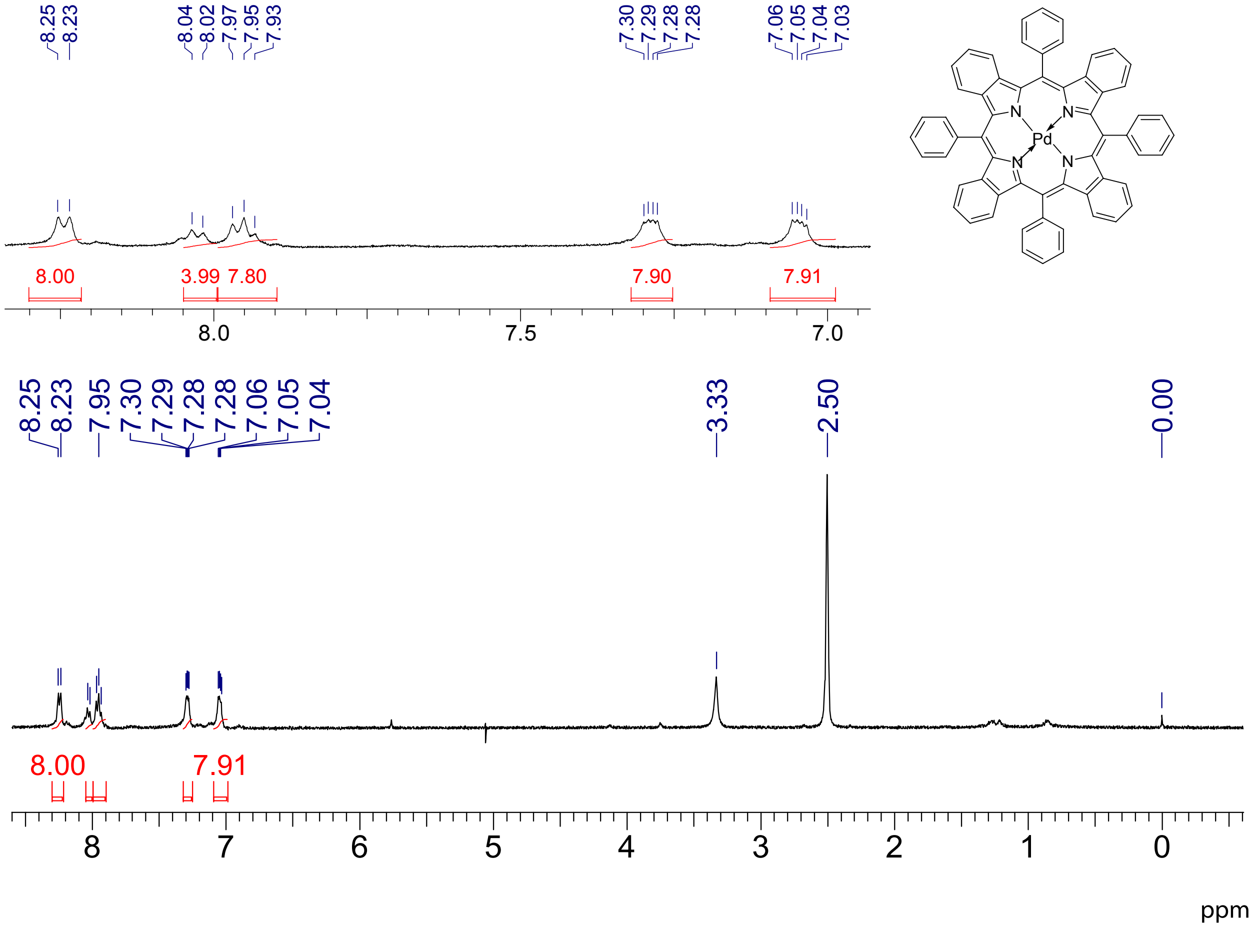


**Fig. S5** $^1$H NMR spectra of **Pd TPTBP** (400 MHz, DMSO-d$_6$).

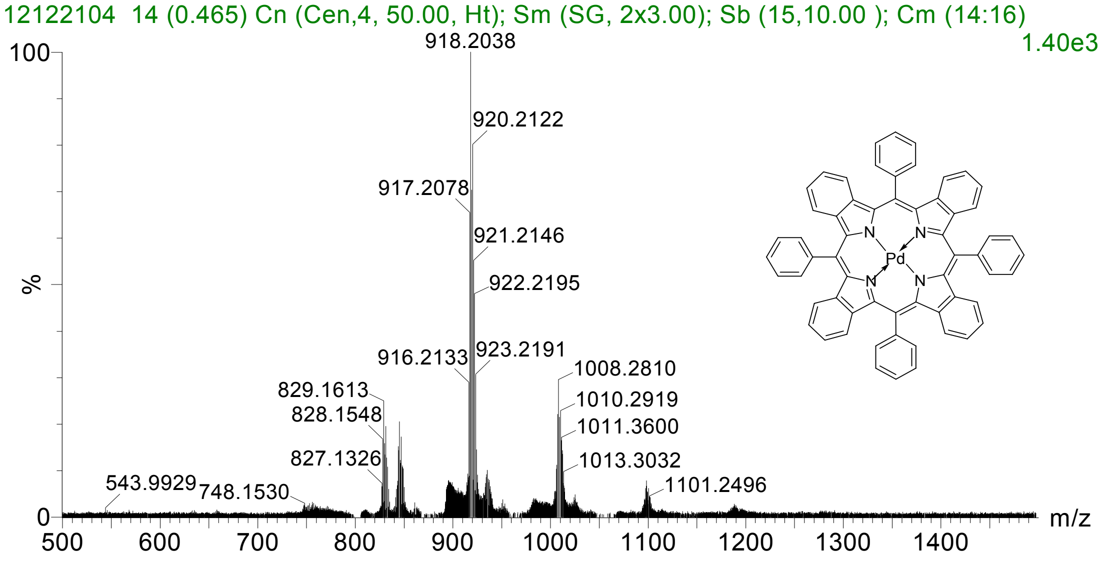


**Fig. S6** MALDI-HRMS of **Pd TPTBP**.

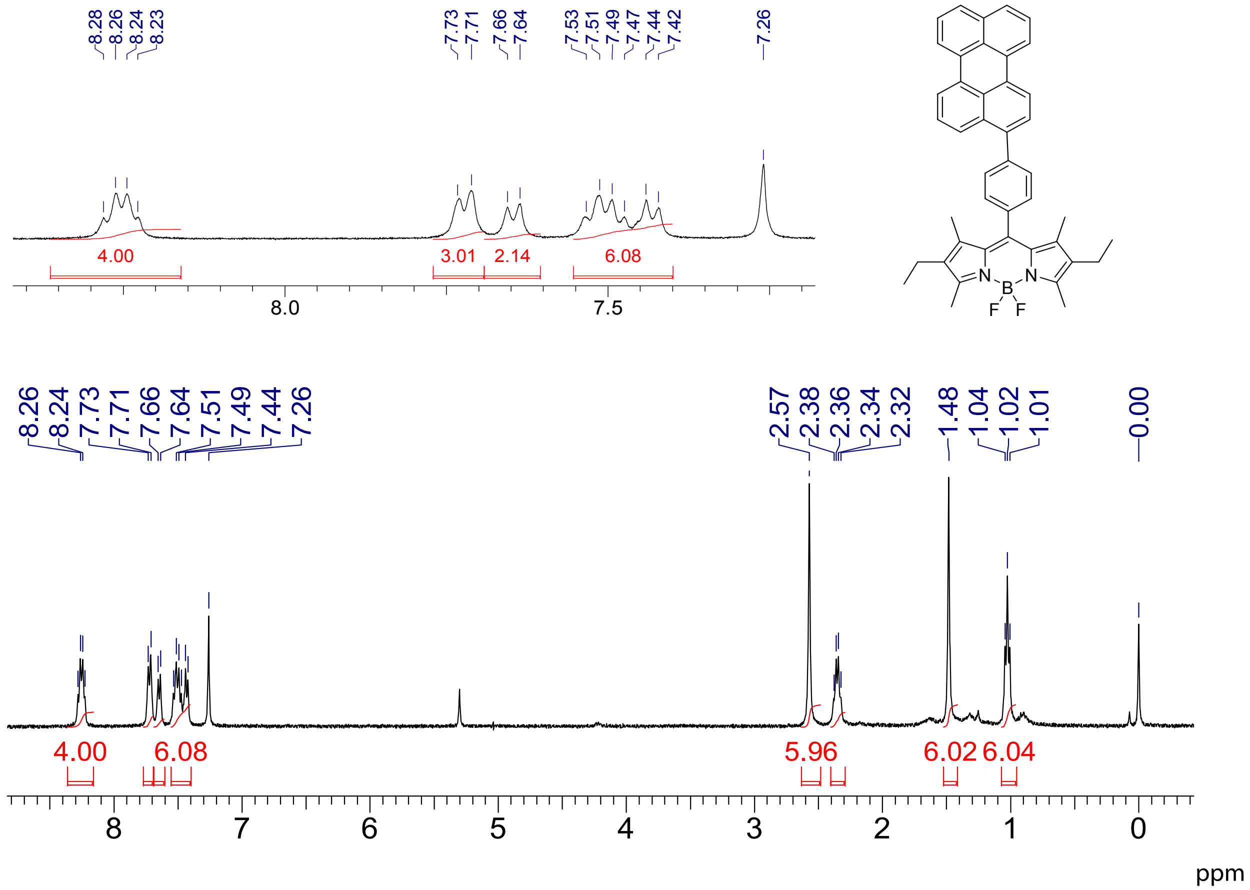


**Fig. S7** $^1$H NMR spectra of **A-1** (400 MHz, CDCl$_3$).

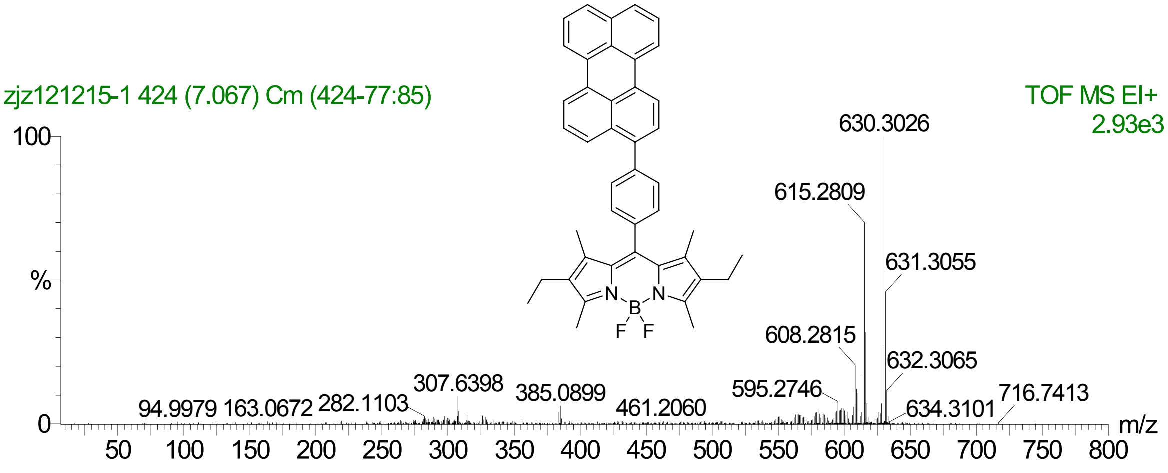


**Fig. S8** EI-HRMS of **A-1**.

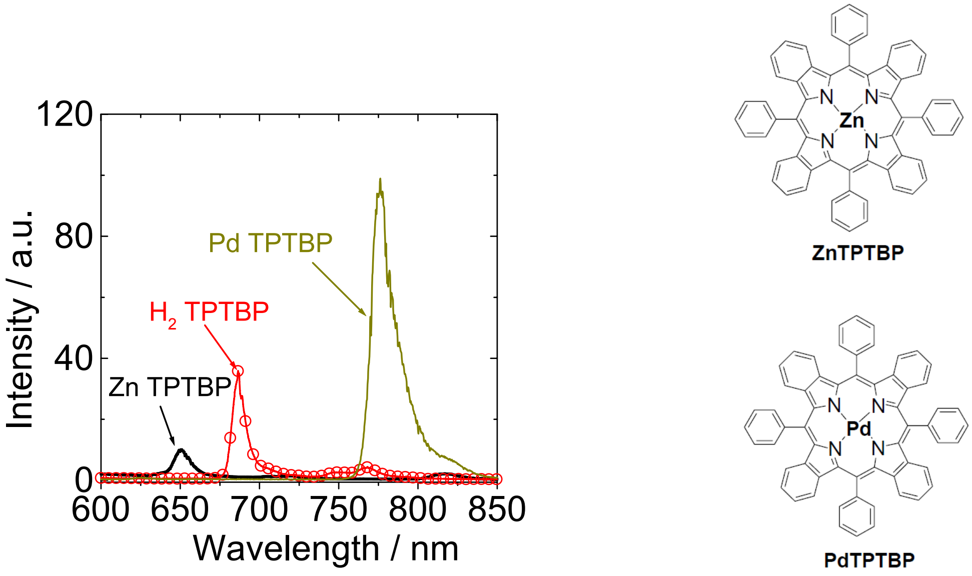


**Fig. S9** Emission spectra of **ZnTPTBP**, **$H_2$TPTBP** and **Pd TPTBP** in ethanol-methanol (4:1, V/V) glass at 77 K. Excitation wavelength: 441 nm. $c = 1.0 \times 10^{-5}$ M.

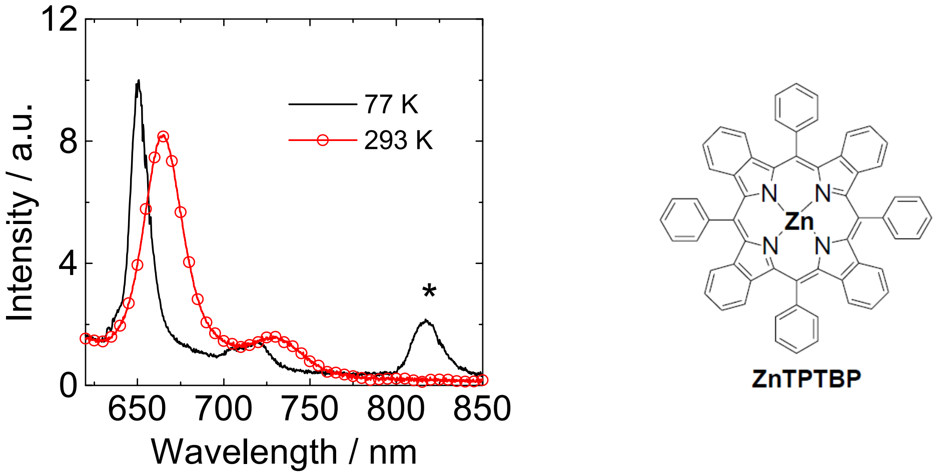


**Fig. S10** Emission spectra of **ZnTPTBP** in ethanol-methanol (4:1, v/v) glass at 77 K and in solution at 293 K. Excitation wavelength was 441 nm. $c = 1.0 \times 10^{-5}$ M. The asterisk indicated the phosphorescence.

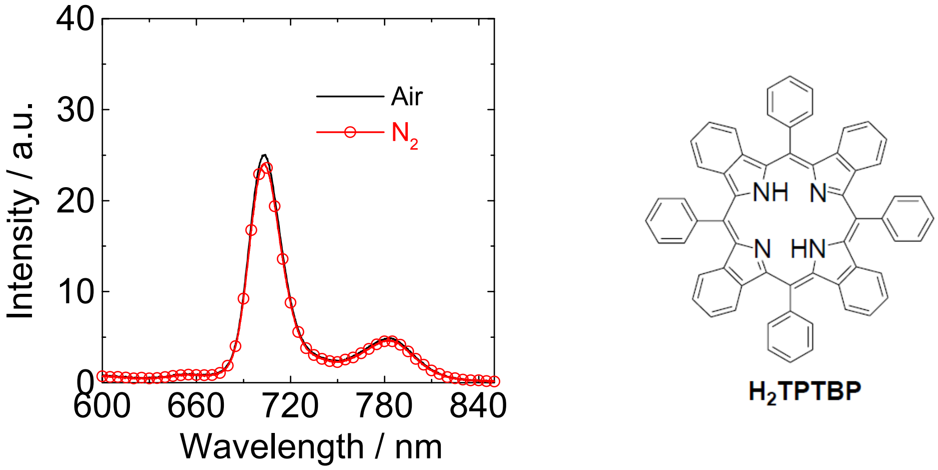


**Fig. S11** Luminescence spectrum of the compounds **$H_2$ TPTBP** in $N_2$ or air-saturated solutions. $\lambda_{ex}$ = 441 nm. $c = 1.0 \times 10^{-5}$ M, in deaerated toluene. 20 °C.

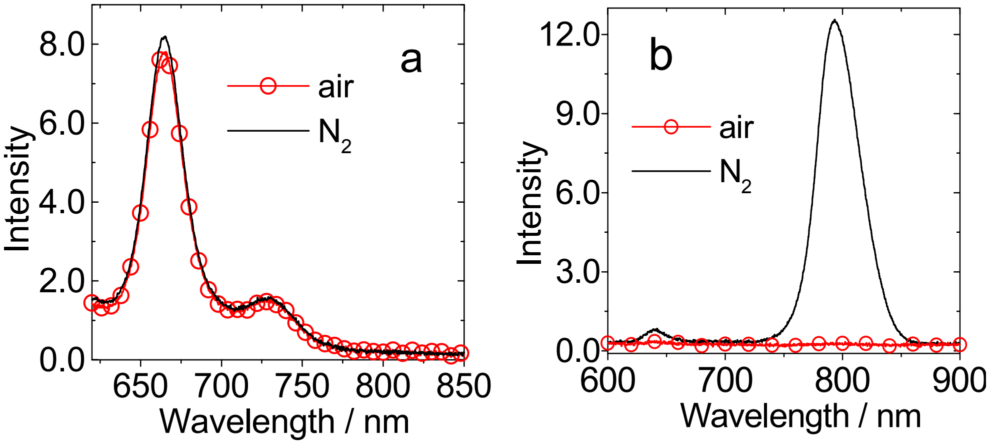


**Fig. S12** Luminescence spectra of (a) ZnTPTBP and (b) PdTPTBP $\lambda_{ex}$ = 441 nm. in $N_2$ or air-saturated toluene ($1.0 \times 10^{-5}$ M; 20 °C). The emission band in (b) at 638 nm is known.

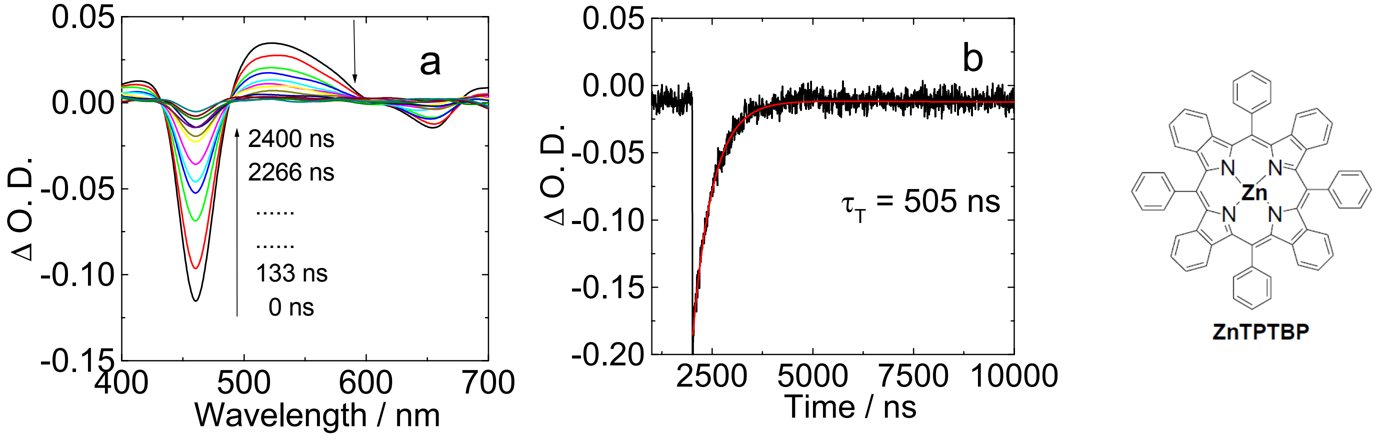


**Fig. S13** (a) Nanosecond time-resolved transient difference absorption spectra of **ZnTPTBP**, (b) decay trace at 470 nm. Excited with 532 nm nanosecond pulsed laser excitation. In aerated toluene ($c = 1.0 \times 10^{-5}$ M, 20 °C).

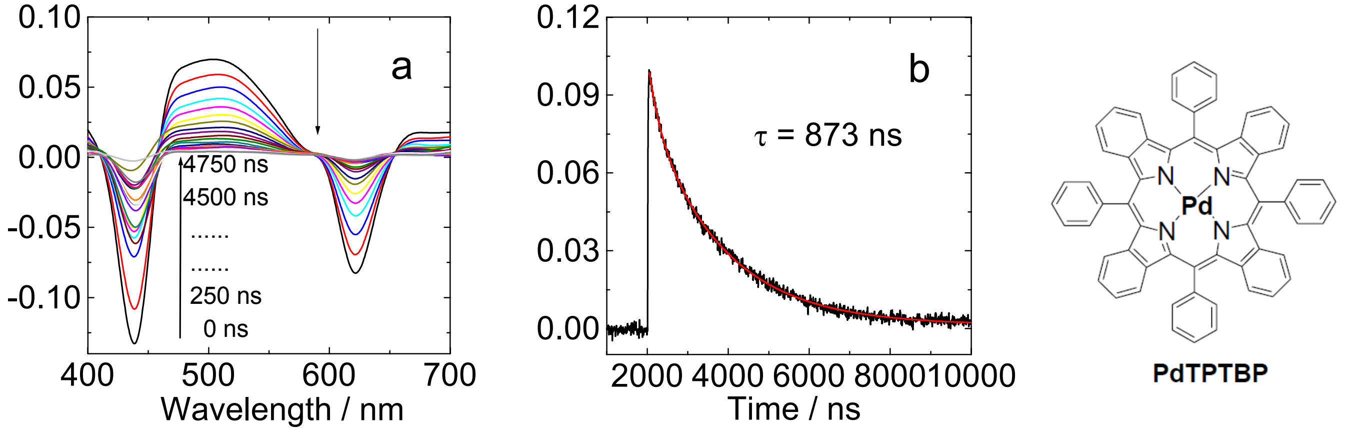


**Fig. S14** (a) Nanosecond time-resolved transient difference absorption spectra of **PdTPTBP**, (b) decay trace at 510 nm; Excited with 532 nm nanosecond pulsed laser excitation. In aerated toluene ($c = 1.0 \times 10^{-5}$ M, 20 °C).

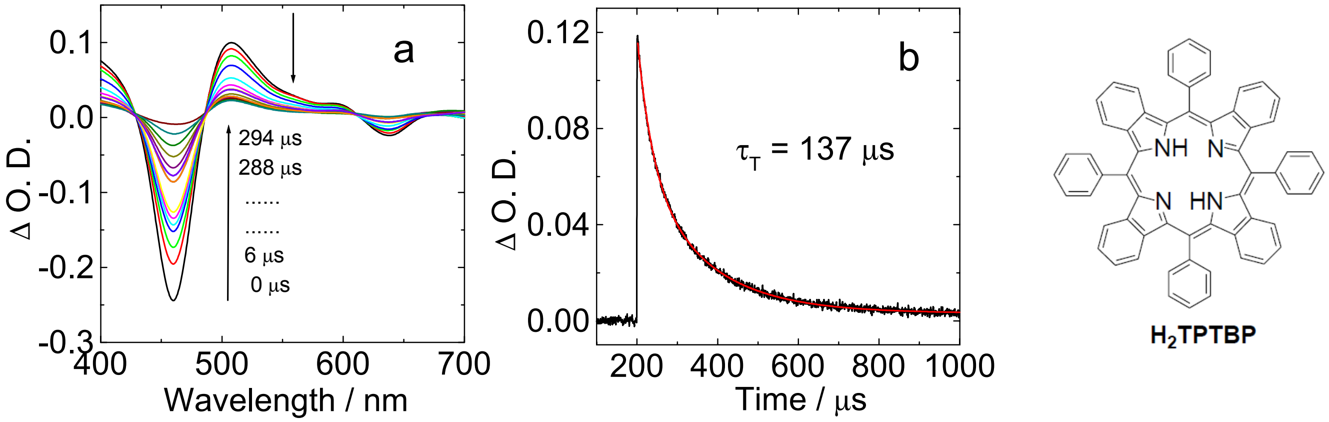


**Fig. S15** (a) Nanosecond time-resolved transient difference absorption spectra of **$H_2$TPTBP**, (b) decay trace at 510 nm; With 532 nm nanosecond pulsed laser excitation. In deaerated toluene (*c* = 1.0 ×$10^{-5}$ M, 20 °C).

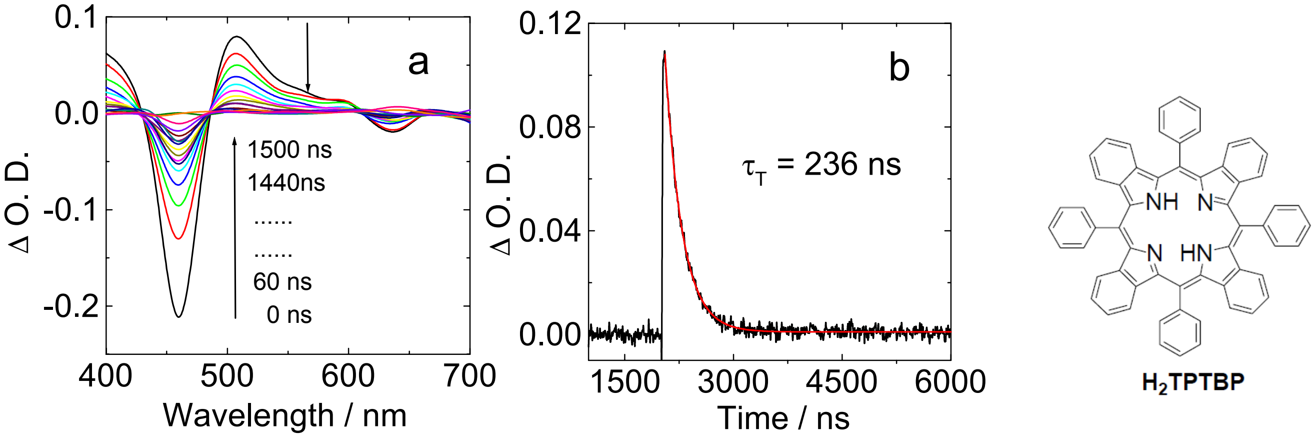


**Fig. S16** (a) Nanosecond time-resolved transient difference absorption spectra of $H_2$TPTBP, (b) decay trace at 510 nm; With 532 nm nanosecond pulsed laser excitation. In toluene (*c* = 1.0 ×$10^{-5}$ M, 20 °C).

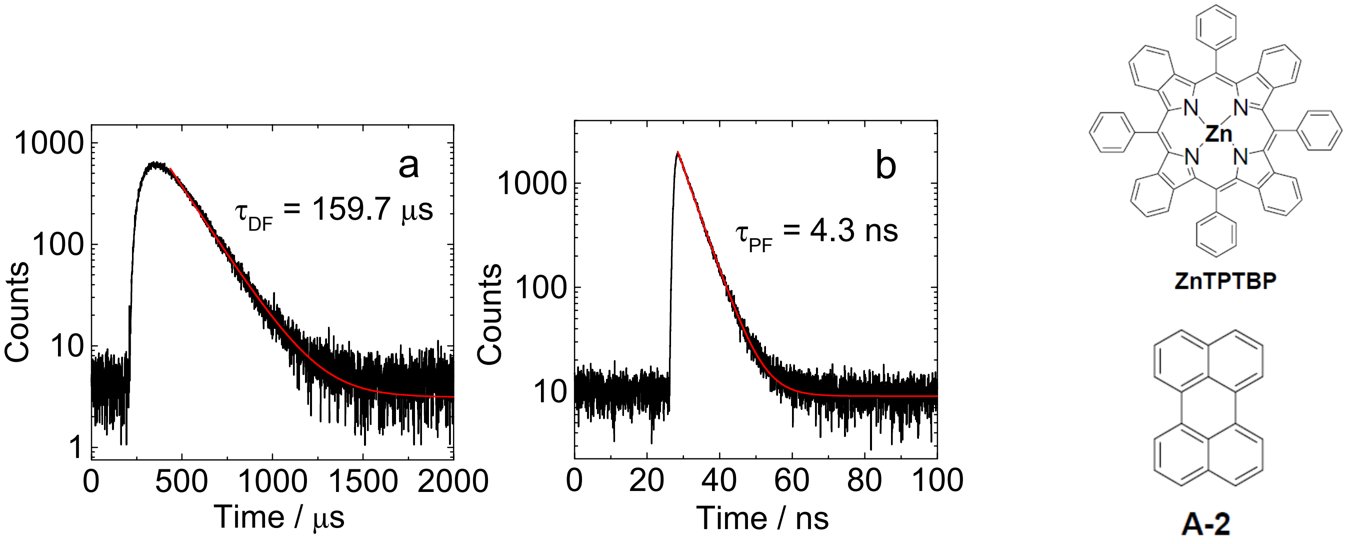


**Fig. S17** (a) Delayed fluorescence observed in the TTA upconversion with ZnTPTBP as the triplet photosensitizer and **A-2** as the triplet acceptor. Excited at 654 nm (nanosecond pulsed OPO laser, synchronized with FLS 920 spectrofluorometer) and the emission was monitored at 450 nm. Under the circumstances, compound ZnTPTBP is selectively excited and the emission is due to the upconverted emission of the triplet acceptor **A-2**. (b) The decay trace of the prompt fluorescence of **A-2** determined in a different experiment (excited with picosecond 405 nm laser; the decay of the emission was monitored at 450 nm). In deaerated toluene; *c* [Photosensitizer]= 2.0 × $10^{-6}$ M; *c* [Triplet energy acceptor **A-2**]= 4.0 × $10^{-5}$ M; 20 °C.

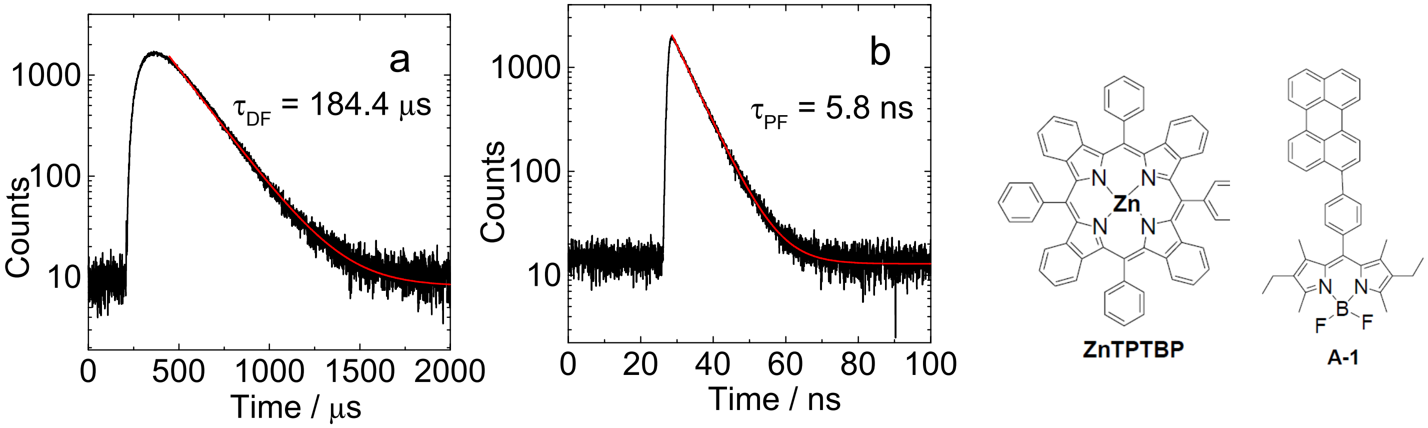


**Fig. S18** (a) Delayed fluorescence observed in the TTA upconversion with **ZnTPTBP** as the triplet photosensitizer and **A-1** as the triplet energy acceptor. Excited at 654 nm (nanosecond pulsed OPO laser synchronized with FLS 920 spectrofluorometer) and the emission was monitored at 545 nm. Under the circumstances, **ZnTPTBP** was selectively excited and the emission is due to the upconverted emission of the triplet acceptor **A-1**. (b) The decay trace of the prompt fluorescence of **A-1** determined in a different experiment (excited with 405 nm picosecond pulsed laser; the decay of the emission was monitored at 545 nm). In deaerated toluene; *c*[Triplet photosensitizers]= 2.0 × $10^{-6}$ M; *c* [Acceptor **A-1**] = 4.0 × $10^{-5}$ M; 20 °C.

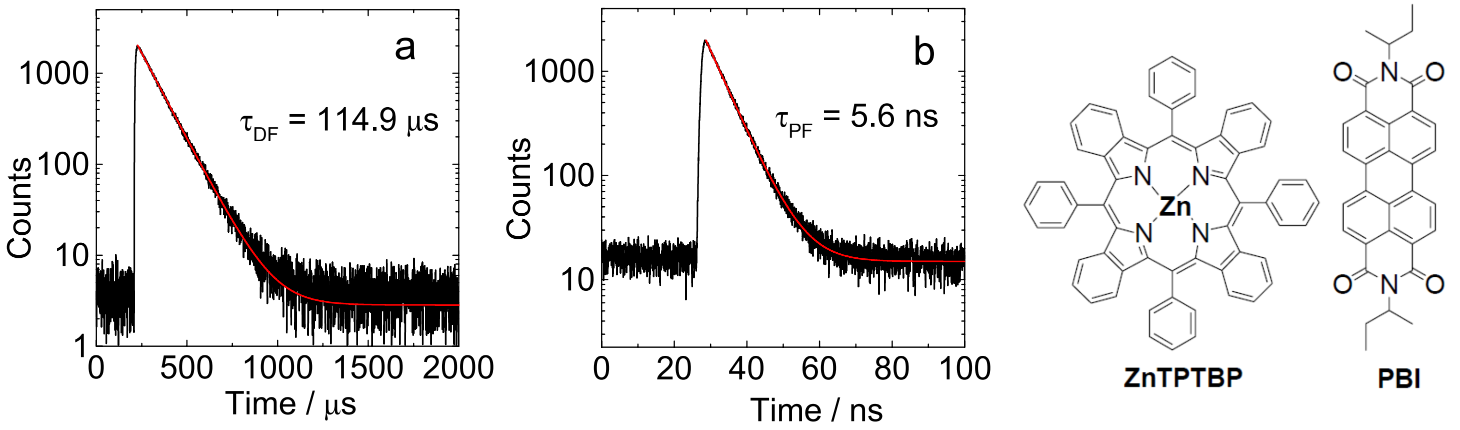


**Fig. S19** (a) Delayed fluorescence observed in the TTA upconversion with ZnTPTBP as the triplet photosensitizer and PBI as the triplet acceptor. Excited at 654 nm (nanosecond pulsed OPO laser synchronized with FLS 920 spectrofluorometer) and the emission was monitored at 539 nm. Under the circumstances, ZnTPTBP is selectively excited and the emission is due to the upconverted emission of the triplet acceptor PBI. (b) The prompt fluorescence decay of PBI determined in a different experiment (excited with 405 nm picosecond pulsed laser; the decay of the emission was monitored at 539 nm). In deaerated toluene; *c*[Triplet photosensitizers]= 2.0 × $10^{-6}$ M; *c* [Triplet energy acceptor **PBI**]= 4.0 × $10^{-5}$ M; 20 °C.

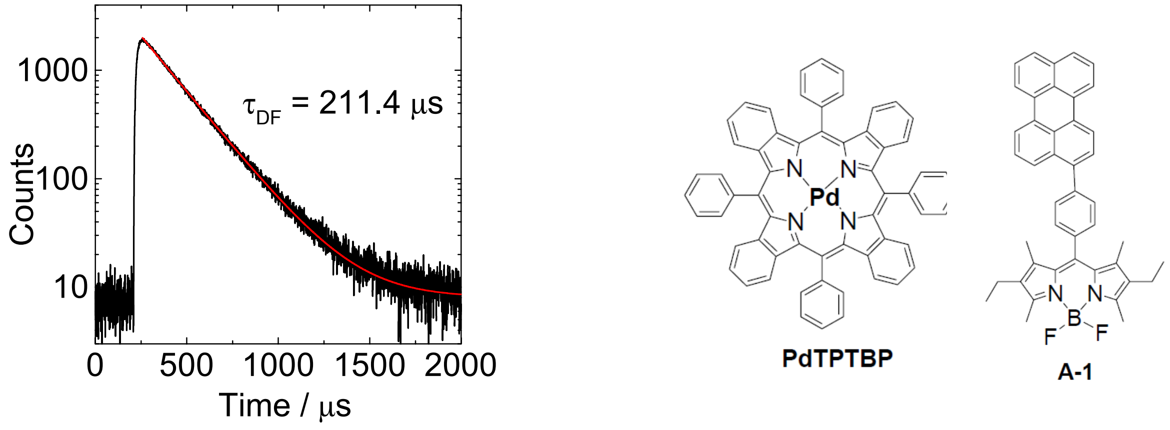


**Fig. S20** Delayed fluorescence observed in the TTA upconversion with PdTPTBP as the triplet photosensitizer and **A-1** as the triplet acceptor. Excited at 654 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and the emission was monitored at 545nm. Under the circumstances, PdTPTBP is selectively excited and the emission is due to the upconverted emission of triplet acceptor. In deaerated toluene; *c*[Sensitizers]=2.0 × $10^{-6}$M; *c* [Acceptor] = 4.0 × $10^{-5}$M; 20 °C.

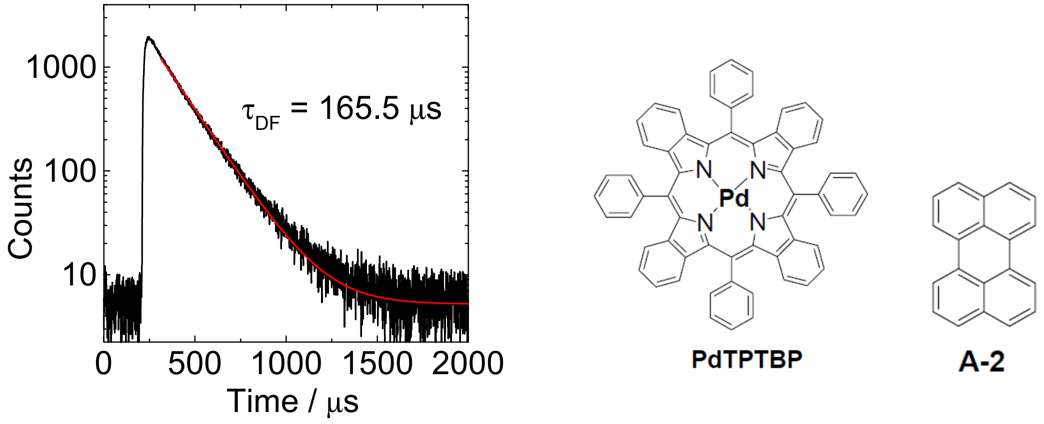


**Fig. S21** Delayed fluorescence observed in the TTA upconversion with PdTPTBP as the triplet photosensitizer and **A-2** as the triplet acceptor. Excited at 654 nm (nanosecond pulsed OPO laser synchronized with FLS 920 spectrofluorometer) and the emission was monitored at 450 nm. Under the circumstances, Pd TPTBP is selectively excited and the emission is due to the upconverted emission of triplet acceptor. In deaerated toluene; *c*[Sensitizers]=2.0 × $10^{-6}$M; *c* [Acceptor] = 4.0 × $10^{-5}$M; 20 °C.

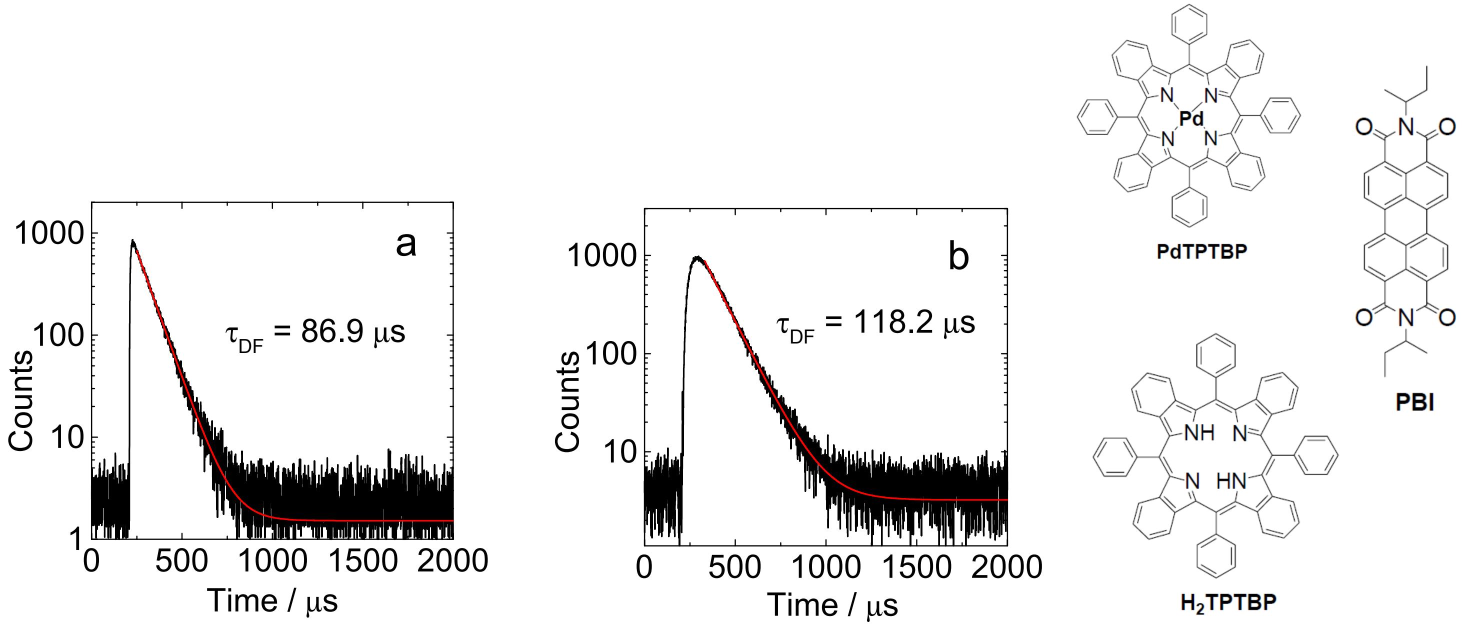
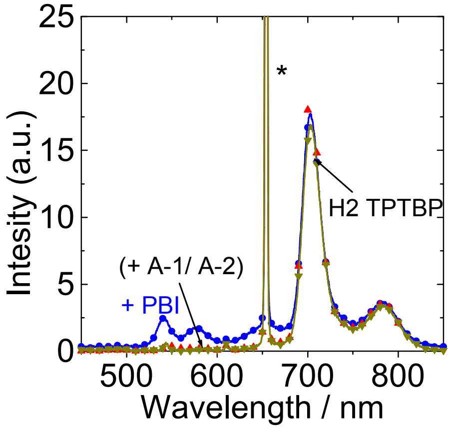


**Fig. S22** Delayed fluorescence observed in the TTA upconversion with compound (a)Pd TPTBP and (b)$H_2$TPTBP as the triplet photosensitizer and **PBI** as the triplet acceptor. Excited at 654 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 539 nm. Under the circumstances, compound is selectively excited and the emission is due to the upconverted emission of triplet acceptor. In deaerated toluene; *c*[Sensitizers]=2.0×$10^{-6}$M; *c* [Acceptor]= 4.0 × $10^{-5}$ M; 20 °C.



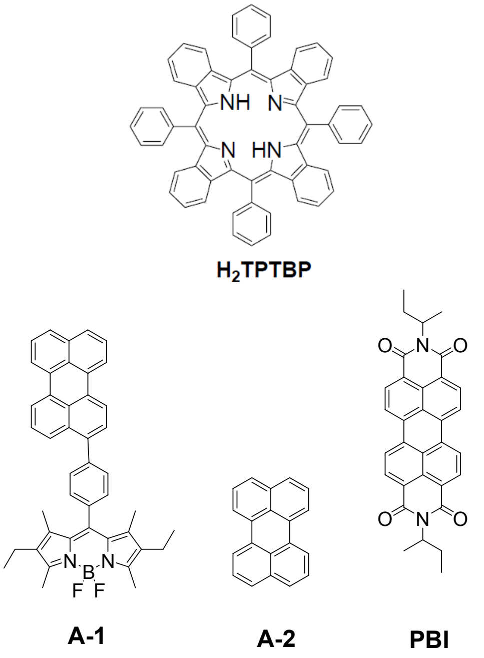
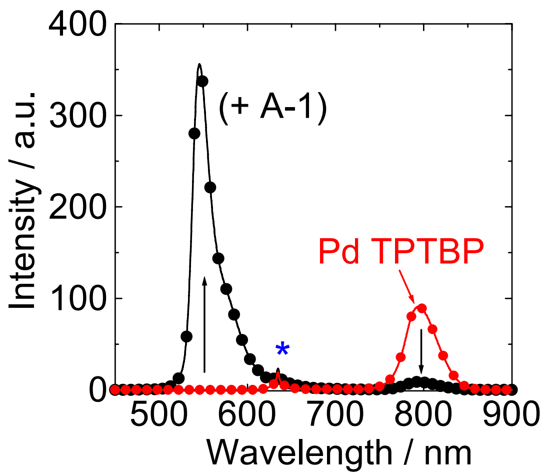


**Fig. S23** Upconversion of $H_2$TPTBP with **A-1**, **A-2** and **PBI** as the triplet acceptor. Excited with 654 nm laser diode (12 mW, 95.5 mW cm$^{-2}$). In deaerated toluene. *c* [Sensitizer] = 2.0 × 10$^{-6}$ M, *c* [Acceptor] = 4.0×10$^{-5}$ M. 20 °C.



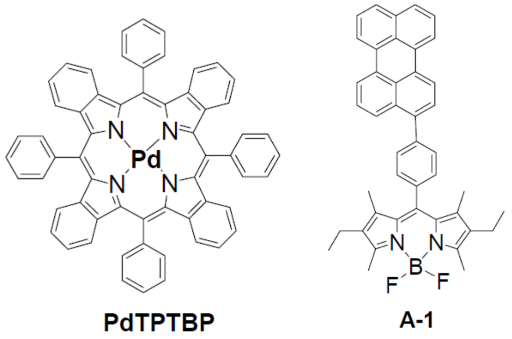


**Fig. S24** Upconversions with triplet photosensitizer **PdTPTBP**. **A-1** was used as triplet acceptor. Emission of the sensitizers in the presence of triplet acceptor **A-1**. Excited with 635 nm laser (4.8 mW). *c* [sensitizer] = 2.0 × 10$^{-6}$ M; *c* [A-1] = 4.0×10$^{-5}$ M; in deaerated Toluene, 20 °C.

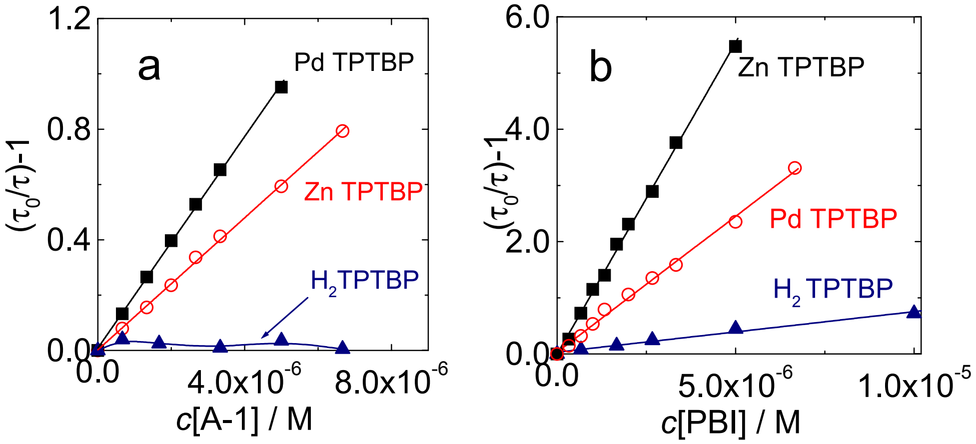
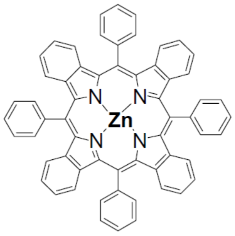
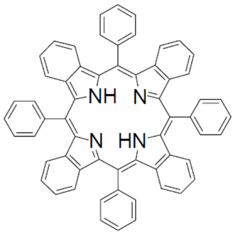


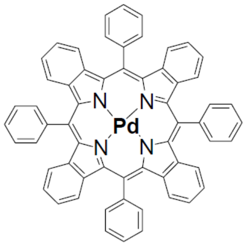
**Fig. S25** The Stern-Volmer plot of ZnTPTBP, $H_2$TPTBP and PdTPTBP with (a) **A-1** and (b) **PBI** as the triplet acceptor. *c* [Sensitizer] = 2.0 × 10$^{-6}$ M. In deaerated toluene. 20 °C. Note the quenching was determined with **A-1** at low concentration.



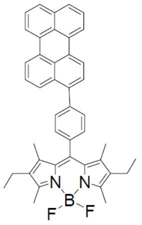
**ZnTPTBP**



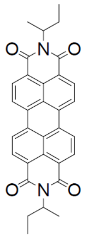
**$H_2$TPTBP**



**PdTPTBP**



**A-1**



**PBI**

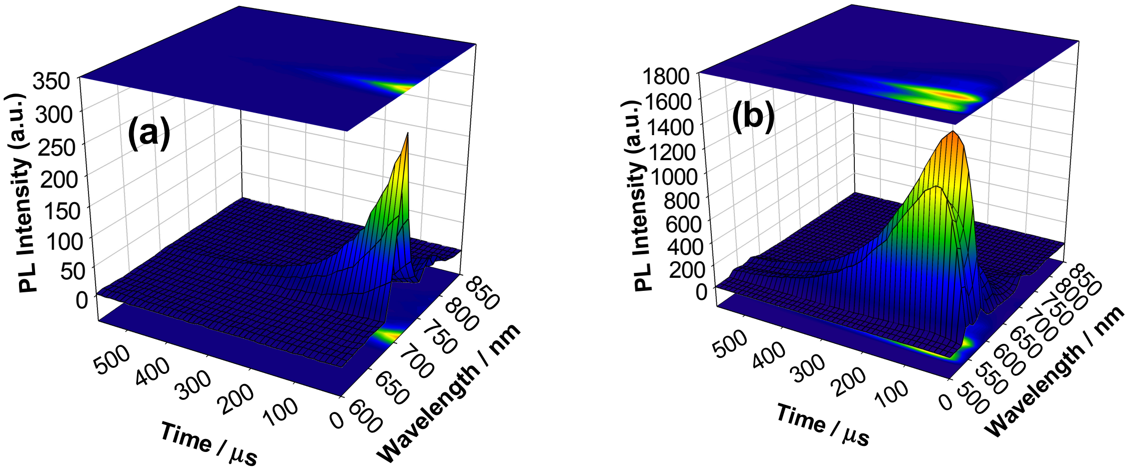
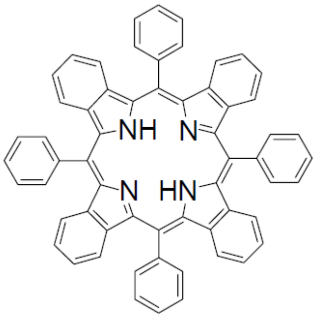
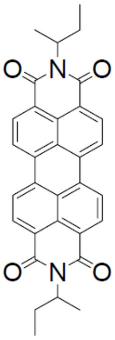


**Fig. S26** Time-resolved emission spectra (TRES) of the TTA upconversion with $H_2$TPTBP as the triplet photosensitizer and **PBI** as the triplet acceptor. (a) $H_2$TPTBP alone, $\tau_F$= 100.6 µs ($\lambda_{em}$ = 700 nm), which is the delayed fluorescence of $H_2$TPTBP. (b) $H_2$TPTBP/PBI upconversion mixture, $\tau_{DF}$ = 122.4 µs ($\lambda_{em}$= 540 nm). Time-resolved emission spectra and intensity decays were recorded using emission mode. The samples were excited using nanosecond pulsed OPO laser (654 nm) *c* [Photosensitizer] = 2.0 × $10^{-6}$ M. *c* [PBI] = 4.0 × $10^{-5}$ M. In deaerated toluene. 20 °C.



**$H_2$TPTBP**



**PBI**

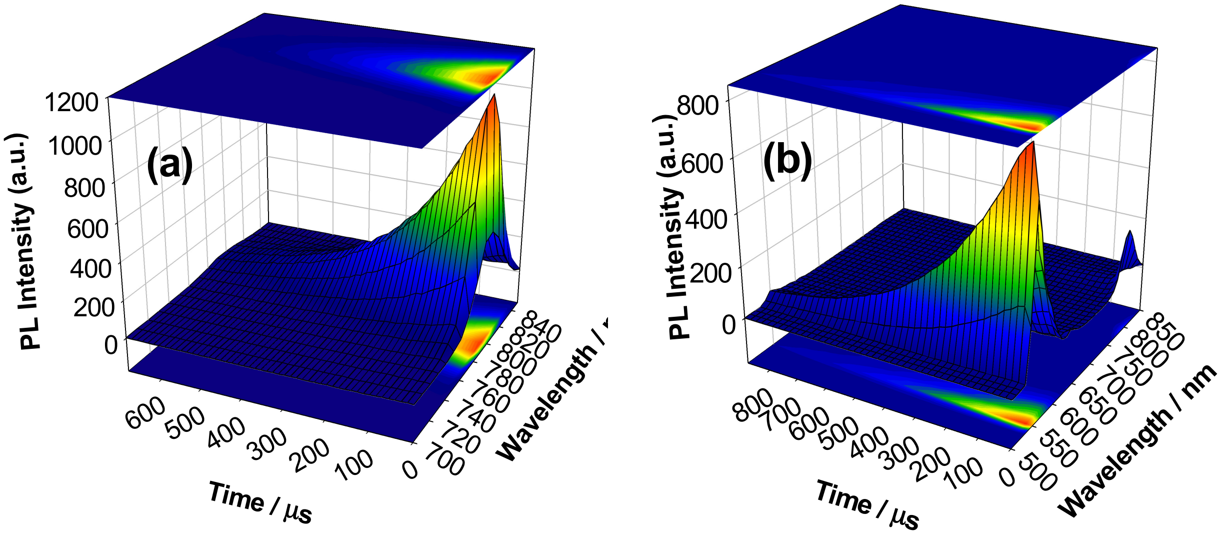
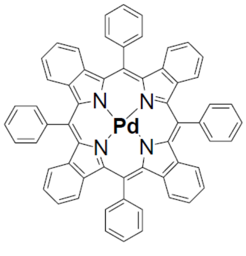
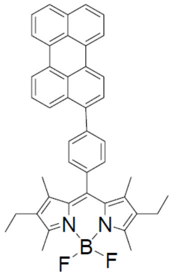


**Fig. S27** Time-resolved emission spectra (TRES) of the TTA UC with **A-1** as triplet acceptor. (a) PdTPTBP alone. $\tau_P$ = 223.7 μs ($\lambda_{em}$= 790 nm). (b) PdTPTBP/**A-1**, $\tau_{DF}$ = 202.5 μs ($\lambda_{em}$= 550 nm). Excited using nanosecond pulsed OPO laser (654 nm). *c* [Photosensitizers] = $2.0 \times 10^{-6}$ M. *c* [**A-1**] = $4.0 \times 10^{-5}$ M in deaerated toluene; 20 °C.



**PdTPTBP**



**A-1**